CHEMISTRY LETTERS, pp. 115-116, 1978. Published by the Chemical Society of Japan

ADDITION OF CARBON TETRACHLORIDE TO CONJUGATED 1,3-DIENES CATALYZED BY DICHLOROTRIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II)[1]

Hideyuki MATSUMOTO, Taichi NAKANO, Toshimi NIKAIDO, and Yoichiro NAGAI

Department of Chemistry, Gunma University, Kiryu, Gunma 376

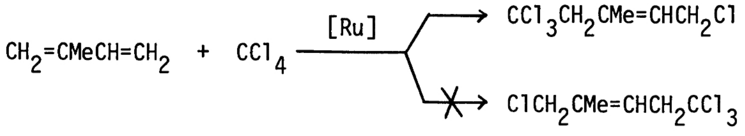
Addition of carbon tetrachloride to conjugated 1,3-dienes such as 1,3-butadiene, 1,3-pentadiene, isoprene, 1,3-cyclohexadiene and 1,3-cyclooctadiene proceeded smoothly under mild conditions in the presence of dichlorotris(triphenylphosphine)ruthenium(II) to give the corresponding 1,4-addition products as 1:1 adducts in excellent yields.

Although much attention has been directed to the addition of carbon tetrachloride across the double bonds of olefins,[2] the addition to conjugated 1,3-dienes has been not yet reported except for one case. Thus, Asscher and Vofsi reported that the addition to 1,3-butadiene was successfully achieved with the use of cupric or ferric chloride as a catalyst to afford the expected 1:1 adduct,[3] However, even in this single example, the use of a cocatalyst and a polar solvent is necessary to attain a satisfactory product yield.[3] We report herein our finding that the addition of carbon tetrachloride to a variety of conjugated 1,3-dienes can be best effected by a homogeneous ruthenium catalyst, dichlorotris(triphenylphosphine)ruthenium(II).[1]

Typically, 8.61g (126 mmol) of 1,3-pentadiene, 65g (420 mmol) of carbon tetrachloride and 0.26g (0.27 mmol) of the ruthenium(II) complex were introduced into a stainless steel vessel. The vessel was then sealed and heated at 80°C for 5 h. The resulting mixture was diluted with 40 ml of n-pentane and the precipitated catalyst was removed by filtration. After evaporation of low boiling materials, distillation gave 23g (82% yield based on the diene charged) of a colorless liquid boiling at 61-62°C (0.4 mm) identified as 1,1,1,5-tetrachlorohexene-3 by its NMR and IR spectra and elemental analysis: NMR (CCl_4) δ 5.83 (m, 2H, -CH=CH-), 4.50 (quintet, 1H, -CHCl-), 3.42 (d, 2H, $-CH_2CCl_3$) and 1.62 (d, 3H, $-CH_3$); IR (neat) 3000-2960, 1645 (C=C), 1500, 1255, 1035, 970 and 905 cm^{-1}; Anal. Calcd for $C_6H_8Cl_4$: C, 32.47; H, 3.63; Cl, 63.90. Found: C, 32.58, H; 3.92; Cl, 63.5.

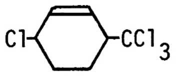
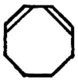
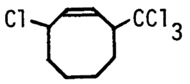
The results of other reactions are summarized in the Table and it is seen that, in all cases, only 1,4-addition products were produced and the yields were excellent. Further, it was found that the addition to isoprene proceeded with a high regioselectivity to give 1,1,1,5-tetrachloro-3-methylpentene-3 only.

$$C{=}C{-}C{=}C \;+\; CCl_4 \xrightarrow{[Ru]} ClC{-}C{=}C{-}CCl_3 \qquad (1)$$



(2)

Table Addition of Carbon Tetrachloride to Conjugated 1,3-Dienes in the Presence of Dichlorotris(triphenylphosphine)ruthenium(II).[a]

Diene	Time (h)	1:1 Adduct[b]	Yield,%[c]
$CH_2=CHCH=CH_2$	4	$ClCH_2CH=CHCH_2CCl_3$	86
$CH_3CH=CHCH=CH_2$[d]	5	$CH_3CHClCH=CHCH_2CCl_3$	82
$CH_2=CMeCH=CH_2$	5	$CCl_3CH_2CMe=CHCH_2Cl$	85
	8		81[e]
	9		83

---

[a] The addition reactions were carried out at 80°C in a sealed stainless steel vessel using a 1:3:0.002 mixture of a diene, the chloride and the ruthenium(II) complex. [b] NMR and IR spectra and elemental analyses were in agreement with the assigned structures. Stereochemistry of the adducts, however, was not determined. [c] Unless otherwise stated, isolated yields are given. [d] A mixture of cis- and trans-isomers was used. [e] Determined by GLC

For comparison purposes, benzoyl peroxide-catalyzed addition reactions of carbon tetrachloride with 1,3-pentadiene, isoprene, 1,3-cyclohexadiene and 1,3-cyclooctadiene were carried out at 80-100°C for 15-24 h in a sealed stainless steel vessel using a 1:5:0.05 mixture of a diene, the chloride and the peroxide. These reactions, however, gave mostly undistillable viscous materials and the yields of the expected 1:1 adducts never exceeded 5%.

In summary, the present results show that the ruthenium(II) complex is an excellent catalyst to initiate the addition of carbon tetrachloride to easily polymerizable 1,3-dienes.

References

1. Radical Reactions in the Coordination Sphere. V. For preceding papers of this series, see (a) H. Matsumoto, T. Nakano and Y. Nagai, Tetrahedron Lett., 5147 (1973); (b) H. Matsumoto, T. Nikaido and Y. Nagai, Tetrahedron Lett., 899 (1975); (c) H. Matsumoto, T. Nikaido and Y. Nagai, J. Org. Chem., **41**, 396 (1976); (d) H. Matsumoto, T. Nakano, K. Takasu and Y. Nagai, J. Org. Chem., in press.
2. For reviews, see (a) C. Walling, "Free Radicals in Solution," Wiley, New York, N.Y. (1957), p.247; (b) C. Walling and E. S. Huyser, Org. React., **13**, 91 (1963); (c) G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry," MacMillan, New York, N.Y. (1964), p.19; (d) Y. Mori and J. Tsuji, Kagaku No Ryoiki, **27**, 197 (1973); (e) F. Minisci, Accounts Chem. Res., **8**, 165 (1975).
3. M. Asscher and D. Vofsi, J. Chem. Soc., 1887 (1963).

(Received December 2, 1977)